14

THE DIELECTRIC PROPERTIES OF MODIFIED LAC

By G. N. BHATTACHARYA

ABSTRACT The measurement of the dielectric properties of two important modified lac compositions, *viz.*, the shellac-urea-formaldehyde resin and the shellac-melamine-formaldehyde resin, have been made over a wide range of temperature and frequency. The result shows that these modified lacs retain the thermoplastic character of lac to a large extent and, therefore, cannot be truly thermosetting. The chemical reaction of these modified lacs have been discussed and it has been suggested that in order to obtain a truly thermosetting resin from lac the long-chain groups of shellac molecule should first be broken to smaller complexes with strongly reactive polar groups so that three dimensional cross-linking may yield the desired result.

INTRODUCTION

A new type of resin is gradually taking its place among the two already existing types *viz.*, natural and synthetic resins. This type of resin has been called 'semi-synthetic' or 'quasi-synthetic' and is usually obtained by modifying a natural resin by means of chemicals so that improved properties towards certain directions are obtained. To this class may be mentioned ester gum and chlorinated rubber. Shellac, although one of the finest and oldest known natural resin, has of late been similarly modified in order to suit itself to the bakelite moulding technique, and to improve upon its heat and water resistance. Amongst these shellac modified with formaldehyde and urea (Venugopalan and Sen, 1939) and with formaldehyde and melamine (Sankaranarayanan and Sen, 1940) have been found to have the best properties so far. These resins have been found to have sufficient thermosetting characteristics so that articles may be moulded and ejected at the same temperature and that has been as high as 140°C-150°C. These, therefore, have sufficient thermo-hardening properties for most practical purposes but are not perfectly thermosetting in the sense that rejected moulded articles of these resins may be recrushed and re-used for further moulding—a fact which has turned to be a decided advantage for the moulding industry. But this fact seems to show that polymerisation of urea or melamine shellac-formal under the usual conditions of manufacture does not progress to such an extent that it can be said to be a perfectly thermosetting resin owing to the development of macro-molecules through cross-linking. Nevertheless, these resins are not truly thermo-plastic since their flow properties are poor compared to most chain polymer-resins and they gradually harden after each moulding operation. According to Sen (1941), these resins are the borderland products between a thermoplastic and a thermo-hardening one. It may be concluded, therefore, that these modified shellac resins are either thermo-hardening resins with insufficiently developed cross-linkages or mixtures which harden at different rates under same conditions. There is apparently no simple way of knowing the nature and extent of changes brought about by the temperature and pressure of moulding except by the Marten's oven test, *i.e.*, by the determination of the softening point of the moulded test bar. The dielectric properties of such resins are expected to be of some help in elucidating the inner mechanism of changes and to some extent the degree of polymerisation. The object of this paper is to report the results of such a study on modified lac resins, which are assuming more and more important positions in the moulding industry.

THEORETICAL

The complex dielectric constant ϵ of a substance in expressed as

$$\epsilon = \epsilon' - i\epsilon''$$

where ϵ' = the real part or the ordinary dielectric constant,
and ϵ'' = the imaginary part or the loss factor.

This loss factor ϵ'' is related to the ordinary dielectric constant ϵ' through a factor, tan δ, which is called power factor, δ being the loss angle ; thus

$$\epsilon'' = \epsilon' \tan \delta$$

The current in phase with the applied voltage

$$I_r = I. \tan \delta = \omega CV. \tan \delta = 2\pi f CV. \frac{\epsilon''}{\epsilon'}$$

But for a parallel plate condenser of area A and thickness d

$$C = \frac{A\epsilon'}{4\pi d 9 \times 10^{11}} \text{ farads}$$

Therefore $$I_r = \frac{fAV\epsilon''}{d \times 18 \times 10^{11}}$$

Now if K_t is the total conductance of this condenser

$$I_r = \frac{AVKt}{d}$$

Equating r.h.s. of these two equations, we have $\epsilon'' = \frac{18 \times 10^{11} \times Kt}{f}$ This is the expression for total loss factor and this includes loss due to d.c. conductance of the material, the measure of which is given similarly by substituting K_o instead of K_t,

i.e., $$\epsilon k_o'' = \frac{18 \times 10^{11}(K_o)}{f}$$

Hence pure a.c. loss is given by

$$\epsilon'' = \frac{18 \times 10^{11}(K_t - K_o)}{f}$$

$$= \frac{18 \times 10^{11} \times K}{f}$$

EXPERIMENTAL

Apparatus.—As reported earlier (Bhattacharya, 1944) a Cambridge Schering bridge and a General Radio radio-frequency bridge were employed at lower and higher frequencies respectively for the determination of dielectric constant and power factor. The power source was a General Radio modulated oscillator type 684-A for high frequencies and a beat frequency oscillator for low frequencies. For 50 c/s a sine-wave alternator was used.

Electrodes.—Tin foil electrodes were used backed by hollow metal electrodes through which oil from a thermostat could be passed by means of a circulation pump. The test specimens were moulded discs of about 4 inch diameter.

Materials.—The materials were all unfilled modified lac resin. The main two composition, *viz.*, shellac-urea-farmaldehyde resin and shellac-melamine-formaldehyde resin, were employed for this study. Other compositions such as shellac-casein (Venugopalan and Sen, 1940a) shellac-coal tar (Venugopalan and Sen, 1940b), shellac-vegetable protein, etc. were not employed since they present a more complicated picture for the study of their structure than the first two and also because they have comparatively less importance in the trade up till now.

Method of procedure.—A few test-discs were moulded out of the compositions using the bakelite moulding technique. Tin foil electrodes were pressed on both the surfaces of a disc using a small quantity of petroleum jelly as adhesive. Hollow metal electrodes were placed on these foil electrodes and oil from a thermostat was circulated through these hollow electrodes in order to keep the disc at any desired temperature. Capacity measurements were made on the bridges when the temperature equilibrium was established. The d.c. conductivity was measured on the same assembly using d.c. voltage and a high sensitivity galvanometer.

CALCULATION

The air capacitance of the test condenser formed by tin foil electrodes was calculated according to Kirchhoff's formula for parallel discs, *viz.*

$$C=\frac{R^2}{4D}+\frac{R}{4\pi}\left[\log_e\frac{16\pi R(Dt)}{D^2}-\frac{t}{D}\log_e\frac{Dt}{t}-3\right]$$

where R = the radius of electrodes in cms.,

t = the thickness of electrodes in cms.,

D = the distance between electrodes in cms.,

and C = capacity of condenser in cms.

The correction for edge capacitance, leads, etc. has been dealt with in a previous paper (Bhattacharya, 1944).

RESULTS

(a) *Shellac-urea-formaldehyde resin*

TABLE I

Dielectric constant-temperature data at different frequencies.

Frequency in Kc/s.	Dielectric constant ϵ' at the temperature of (°C)							
	30°	40°	50°	60°	70°	80°	90°	100°
500	4.81	5.07	5.40	5.69	5.95	6.18	6.19	6.26
100	4.95	5.24	5.62	5.97	6.25	6.63	6.63	6.63
50	5.07	5.38	5.71	6.11	6.47	6.80	6.90	6.87
10	5.14	5.47	5.95	6.47	6.99	7.46	7.46	7.10
1.0	5.38	5.76	6 42	7.18	7.99	9.03	9.41	8.85
0.05	5.40	5.92	6.86	8.34	9.96	—	—	—

TABLE II

Measured power factor data at various temperatures and frequencies.

Frequency in Kc/s.	Measured power factor at the temperature of (°C)							
	30°	40°	50°	60°	70°	80°	90°	100°
500	.0319	.0336	.0358	.0415	.0493	.0574	.0612	.0656
100	.0184	.0291	.0335	.0420	.0589	.0668	.0721	.0747
50	.0235	.0292	.0378	.0506	.0566	.0744	.0754	.0911
10	.0136	.0290	.0434	.0600	.0787	.0950	.1088	.1050
1.0	.0321	.0412	.0545	.0666	.0931	.1137	.1870	—
0.05	.0240	.0440	.0900	.1800	—	—	—	—

TABLE III

Corrected dielectric loss—temperature data

Frequency in Kc/s.	Dielectric loss ϵ'' at the temperature of (°C)							
	30°	40°	50°	60°	70°	80°	90°	100°
500	.153	.170	.193	.236	.293	.354	.374	.378
100	.091	.153	.188	.250	.373	.438	.462	.457
50	.119	.157	216	.309	.363	.496	.487	.423
10	.071	.159	.257	.385	.536	.659	.647	.394
1.0	.173	.237	.345	.450	.603	.526	.104	—
0.05	.120	.255	532	.910	—	—	—	—

(*b*) *Shellac-melamine-formaldehyde resin*

TABLE IV

Dielectric constant-temperature data at different frequencies.

Frequency in Kc/s.	Dielectric constant at the temperature of (°C)							
	30°	40°	50°	60°	70°	80°	90°	100°
500	4.78	5.10	5.37	5.79	6.11	6.34	6.16	5.96
100	5.00	5.32	5.67	6.14	6.56	6.81	6.61	6.31
50	5.10	5.40	5.79	6.31	6.78	7.05	6.86	6.53
10	5.22	5.62	6.09	6.61	7.20	7.45	7.48	7.00
1.0	5.57	5.99	6.86	7.60	8.69	9.40	9.50	9.00
0.05	5.61	6.31	7.85	9.59	11.21	—	—	—

TABLE V

Measured power factor data at different temperatures and frequencies.

Frequency in Kc/s.	Power factor (uncorrected) at the temperature of (°C)							
	30°	40°	50°	60°	70°	80°	90°	100°
500	.0424	.0453	.0477	.0514	.0589	.0643	.0645	.0624
100	.0343	.0365	.0453	.0530	.0641	.0700	.0688	.0705
50	.0304	.0308	.0496	.0601	.0645	0671	.0731	.0804
10	.0331	.0392	.0502	.0671	.0841	.1040	.1280	.2020
1.0	.0459	.0608	.0783	.0964	.1260	—	—	—
0.05	.0380	.0980	.2100	—	—	—	—	—

TABLE VI

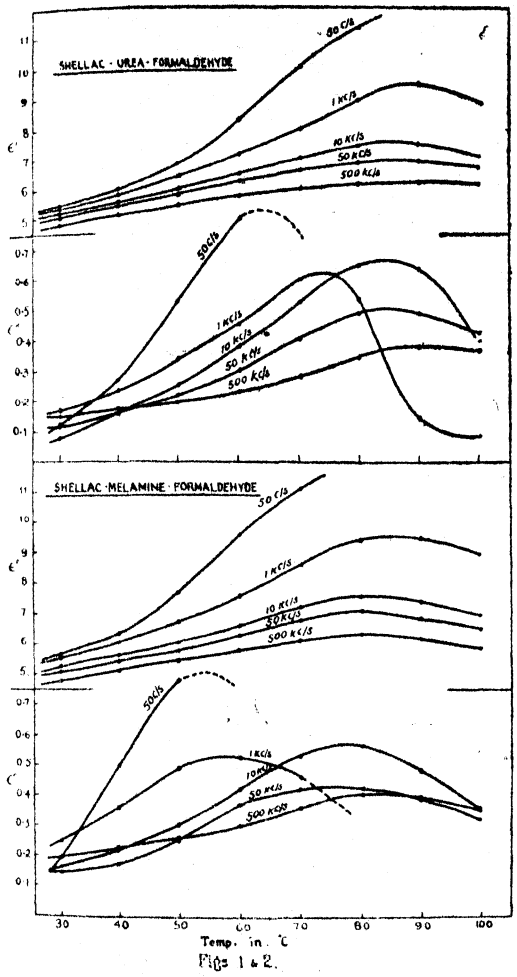
Corrected dielectric loss—temperature data

Frequency in Kc/s.	Dielectric loss at the temperature of (°C)							
	30°	40°	50°	60°	70°	80°	90°	100°
500	.203	.231	.256	.298	.359	.403	.388	.352
100	.171	.194	.256	.323	.413	.456	.408	.342
50	.155	.166	.257	.375	.423	.433	.407	.320
10	.173	.220	.301	.422	.531	.569	.489	.360
1.0	.255	.359	.493	.520	.458	—	—	—
0.05	.200	.510	.780	—	—	—	—	—

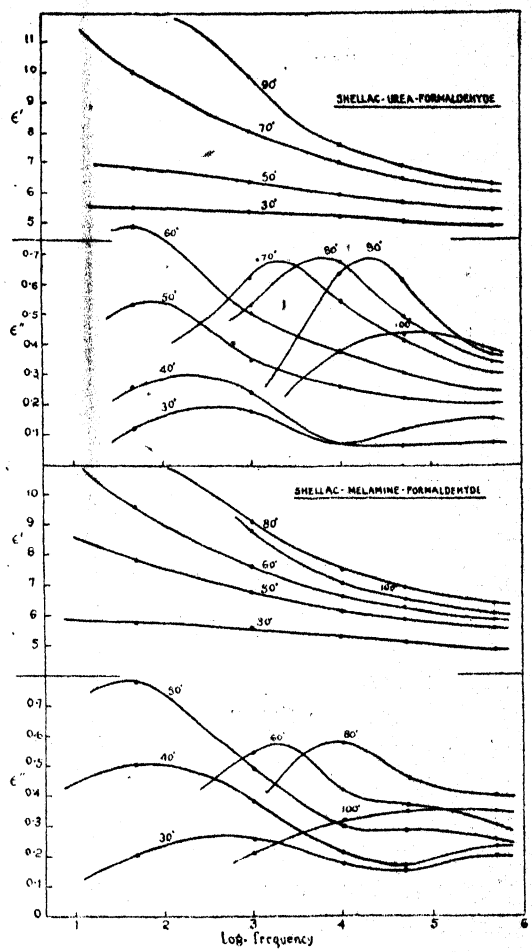
DISCUSSION

The dielectric constant-temperature curves of figures 1 & 2 should be observed carefully. Fig. 1 shows curves for shellac-urea-formaldehyde in respect of ϵ' and ϵ'' whilst Fig. 2 for shellac melamine-formaldehyde. It may be seen that the maximum value of dielectric constant for any frequency decreases as the frequency increases. In fact the maximum value of ϵ', which is attained between the temperature range of 80°C to 90°C for practically all the frequencies, is near about 6 at 500 Kc/s and more than double this figure at 50 c/s. This suggests that shellac molecule with the interposition of formaldehyde and urea or melamine has increased so much in size that it becomes less and less probable for it to orient in response to the increasing frequency of the alternating field owing to its large time of relaxation. If it is considered, however, that the whole molecule does not take part in the rotation, the explanation may be that the polar groups, responsible for loss in lac, are bound up in such a way with cross-linking forces under this reaction that their freedom of movement is very much restricted. With the decrease of frequency of the applied field more and more molecules of polar groups can contribute towards the increase of the dielectric constant by aligning themselves as far as possible along the field. From this we also see that cross-linking has not developed in this reaction to such an extent that orientation of individual molecule or rotation of polar groups becomes altogether impossible. In fact these resins are not truly thermo-setting and, although diminished to a great extent,

they have still retained their thermoplastic character. This will be more evident if we scrutinise the loss factor—temperature curves of both of them. It will be seen that up to 10 Kc/s the



Figs 1 & 2.



Figs. 3 & 4.

maxima of loss curves appear in the order in which they are expected for a thermoplastic resin. After 10 Kc/s, the value of the maximum gradually diminishes and its position also shifts but slightly. The picture that can be drawn at once to explain such a behaviour is the same as has been depicted above. The rotating unit is large or more possibly bound up with cross-linkages to a large extent and is not free to take up positions in response to the applied field. The internal viscosity has also increased to a great extent since the material does not melt but softens very slightly at high temperatures, the softening being manifested by the loss of its elasticity only. But still its thermoplastic character is not altogether destroyed and this is clearly manifested by its dielectric properties. Measurements at 50 c/s could not be pursued over the Schering bridge above 50°C or 60°C since the sensitivity of the bridge decreased immensely with the increase of power factor of the material. But the readings were sufficient to reveal the character of the curves.

The frequency-dielectric constant or loss factor (Figs. 3 & 4) curves also bring out the same conclusions. If we examine loss-frequency curves of shellac-urea-formaldehyde we

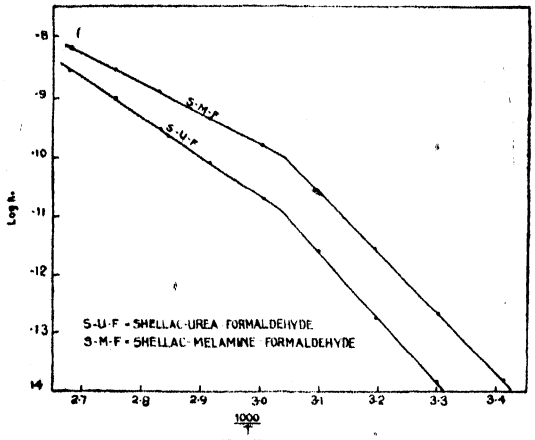


Fig.5.

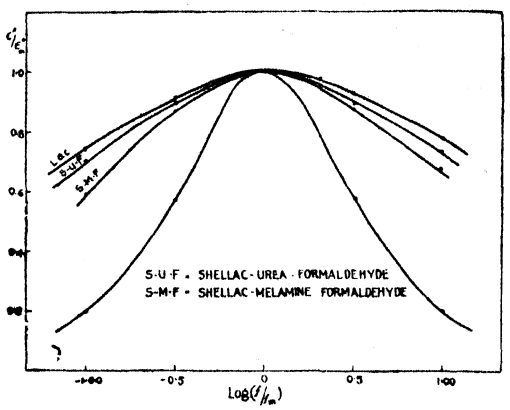


Fig.6

shall find that after 60°C the character of a polar thermoplastic resin is noticeable although there is no outward melting of the resin or even softening. At temperatures lower than 60°C the three dimensional forces are more prominent and as a result the loss-maximum decreases gradually with the fall of temperature without any appreciable shift of position. In the case of shellac-melamine-formaldehyde resin also the same behaviour is noticeable but probably the inner change of state starts a bit earlier—the magnitude of which may not be more than a few degrees only.

In order to throw more light on the question of inner change of state the indirect method of d.c. conductance measurement gave some important information, since it was not possible to apply the direct method of measuring plasticity or viscosity at different temperatures. It may be seen that two straight lines are obtained if log d.c. conductance values are plotted against the reciprocal of absolute temperature for any of these modified lac resins (Fig. 5) and they meet at a point which corresponds to near about 55°C. It must be understood, however, that actually this point may not be so sharp but probably the change of state takes place over a small range of temperature between 50°C and 60°C. In the case of whole lac a similar behaviour was noticed (Bhattacharya, 1944) and a break was observed in the log $K_0 - 1/T$ line at about 60°C, with the difference that there the inclination of the line with $1/T$ axis was less after 60°C whereas it is more here. The activation energies calculated from these slopes are naturally very different, showing that some fundamental change has taken place in the molecule. In fact the activation energy of shellac-urea-formaldehyde at temperatures higher than 60°C is 30.4 K-cal and lower than 50°C is 50.1 K-cal whilst the same for shellac-melamine-formaldehyde are 23.6 K-cal and 46.0 K-cal respectively. This difference is not much and from these considerations it can be said that the nature of reaction in both shellac-urea-formaldehyde and shellac-melamine-formaldehyde is the same. But there is very little coincidence between the log-conductance—$1/T$ line of whole lac and of these modified lacs except that the break occurs at about the same place. It may be that near about this temperature some inner change of state due to weakening of inter-molecular forces occurs and this peculiarity of lac is retained even when lac is modified with formaldehyde and urea or melamine since the main structure of lac is not destroyed by such reactions.

TABLE VII

D.C. conductance—temperature data of shellac-urea-formaldehyde

Temperature		$1/T \times 10^3$	D. C. conductance K_0	log K_0
t°C	T°K			
30°	303	3.300	1.50×10^{-14}	−13.824
40°	313	3.196	1.62×10^{-13}	−12.790
50°	323	3.096	2.38×10^{-12}	−11.623
60°	333	3.003	1.55×10^{-11}	−10.810
70°	343	2.915	7.81×10^{-11}	−10.107
80°	353	2.833	2.77×10^{-10}	−9.558
90°	363	0.755	9.20×10^{-10}	−9.036
100°	373	2.681	2.15×10^{-9}	−8.668

TABLE VIII

D.C. conductance-temperature data of shellac-melamine-formaldehyde

Temperature		$1/T \times 10^3$	D.C. conductance K_0	Log K_0
t°C.	T°K			
25°	298	0.356	5.16×10^{-14}	−13.288
30°	303	3.300	1.85×10^{-13}	−12.733
40°	313	3.195	3.00×10^{-12}	−11.513
50°	323	3.096	2.45×10^{-11}	−10.611
60°	333	3.003	1.18×10^{-10}	−9.928
70°	343	2.915	4.13×10^{-10}	−9.384
80°	353	2.833	1.14×10^{-9}	−8.943
90°	363	2.755	2.60×10^{-9}	−8.585
100°	373	2.681	5.71×10^{-9}	−8.244

According to Sen (1941), a shellac formal is formed by the interaction of shellac with formaldehyde and this formal is more plastic than lac itself. It has also got the property of slower polymerisability under heat. The mechanism of action of urea on this formal has been expressed by him to be of a condensation type with the elimination of water. The introduction of formal grouping has increased the reactivity of the rather inert lac molecule. The mechanism of reaction of melamine with shellac formal is also similar and is brought about through the amino-groups, as in the case of urea. But the plot of ϵ''/ϵ''_m against f/f_m reveals some interesting and unexpected facts. The higher softening points and thermosetting properties of these modified lacs would at first sight suggest that these resins would have very wide distribution range of relaxation times of the molecule. But actual plot in Fig. 6 shows that the shellac-melamine-formaldehyde resin has a lower distribution range than the corresponding urea resin and that both of them have lower range of distribution of relaxation times than lac itself. This is rather surprising but not improbable if it is considered that the introduction of aldehyde, amino and other polar groups in place of a few hydroxyls has, in fact, concentrated the distribution instead of dispersing it. The whole molecule does not evidently rotate but these different polar groups contribute towards the dielectric loss. The distribution naturally depends upon their individual relaxation time and their freedom of rotation which again is

dependent upon their position in the molecule. We have already seen (Bhattacharya, *loc. cit.*), that the hydroxyl groups are the main rotating units in the case of whole lac ; evidently their position on the body of the molecule and hence their freedom to rotate determines the distribution. It is probable, therefore, that by introducing formal grouping and then amino groups through urea or melamine the effect of distribution becomes less since they are all concentrated near a few fixed spots and so their chances to act collectively as a single unit are more. It should be remembered that the execution of complete rotation by the polar body is not necessary for dielectric polarisation but movement from one position to another by turning through a small angle is usually sufficient. It is difficult to depict the true picture of the rotating polar units in these semi-synthetic resins, since the structure of the main body, *viz.* lac resin, is not yet known and the knowledge regarding this is far from satisfactory at the present moment. All that we can say with definiteness now is that the lac molecule contains five hydroxyl groups and that aleuritic acid, 9, 10, 16 trihydroxypalmitic acid, must be one of its main constituents, since it can be obtained in good yield on hydrolysis of lac by strong caustic alkali. This acid is an open chain fatty acid of simple structure, containing 16 carbon atoms like palmitic acid with the addition of three hydroxyls at the positions indicated above. There is sufficient evidence to show that urea (Bhattacharya, 1940) or melamine (Sankarnarayanan and Sen, 1944) reacts at the carboxyl of lac and not at the free hydroxyls, but when shellac formal is formed by the interaction of formaldehyde it reacts at the formal grouping and not at the carboxyl (Sen, 1941). If only the aleuritic acid part of the structure of lac is considered it can be said that the formal and amino groups are on the side chain and hence are in a position to execute vibrations better than if they had been on the main chain. This fact probably explains the more thermoplastic character of lac formal also.

One thing, however, is very clear from this dielectric study, *viz.*, the thermoplastic character of lac, which is usually believed to be due to its having long chain groups in the molecular structure (Houwink, 1934), is not destroyed in these so called thermo-hardening reactions. This is to be expected since most of these reactions take place only at free carboxyls at the end of the chain-structure. In order to make, therefore, a truly thermo-setting resin from shellac the long molecule should first be broken up into simpler complexes so that cross-linking may yield a really hardened product.

ACKNOWLEDGMENT

The author wishes to record his deep sense of gratitude to Dr. H. K. Sen, Director of this Institute, for his kind interest in this work.

PHYSICAL AND PHYSICO-CHEMICAL LABORATORIES,
INDIAN LAC RESEARCH INSTITUTE, NAMKUM, RANCHI.

REFERENCES

Bhattacharya, G. N., 1940, *Ind. Lac. Res. Inst.* Bull. **42**.
,, ,, 1944, *Ind. J. Phys.*, **18**. 1.
Houwink, R., 1934, *Akid. Vetage* **187**.
Sankaranarayanan, Y. and Sen, H. K., 1940, *Ind Lac. Res. Inst.* Note 22.
,, ,, ,, ,, ,, 1944, ,, ,, ,, ,, 21.
Sen, H. K., 1941, *J. Ind. Chem. Soc.* **18**, 47.
Venugopalan M., and Sen, H. K., 1939, *British Plastics*, **10**, 626.
,, ,, ,, ,, ,, 1940(*a*), *Ind. Lac. Res. Inst.* Note 21.
,, ,, ,, ,, ,, 1940(*b*), ,, ,, ,, ,, 23.